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(54) Process for Delignifying Lignocellulose Material

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Process for delignifying lignocellulose material

Abstract of the disclosure

A process for delignifying lignocellulose material by a chemical pulping process. The process is carried out at a liquor ratio of 1:3 to 1:50, in the presence of a thioamide, thiocarbamide, thiocarbamate or dithiocarbamate, advantageously with the concurrent use of an organic cyclic compound containing keto and/or hydroxyl groups, in particular anthraquinone or 2-methyl-anthraquinone.

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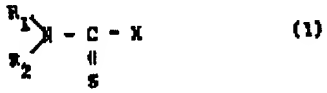
Case 1-13074/4

Process for delignifying lignocellulose material

The present invention relates to a process for delignifying lignocellulose material, e.g. wood, straw, cane, begasse, hemp and the like, by means of a chemical pulping process. The process comprises carrying out the pulping at a temperature up to 250°C in the presence of an effective amount of a thioamide, thiocarbamide, thiourbamate or dithiocarbamate, wherein the ratio of the lignocellulose material to the pulping liquor is in the range of 1:3 to 1:50.

The thiocarbamides and dithiocarbamides are both cyclic and, preferably, acyclic compounds. Acyclic thioureas are especially preferred.

Preferred compounds are those of the formula



(1)

wherein X is alkyl of 1 to 12 carbon atoms, cycloalkyl, aryl, aralkyl,  , -OM or -SM, each of R_1, R_2, R_3 and R_4 independently is hydrogen, alkyl of 1 to 12 carbon atoms, lower alkoxy-lower alkyl, phenyl, benzyl, or phenyl or benzyl substituted by halogen, lower alkyl, lower alkoxy, lower alkoxy-lower alkyl or sulfo, or each pair of substituents (R_1 and R_2) and (R_3 and R_4) independently, together with the nitrogen atom to which said pair is attached, is a 5- or 6-membered heterocyclic radical, or R_1 and R_3 together are alkylene

of 2 or 3 carbon atoms or phenylene, and M is a cation.

In the definition of the radicals of compounds of the formula (1) and of the subsequent formulae, lower alkyl and lower alkoxy will normally be understood as denoting those groups or group components which contain 1 to 5, preferably 1 to 3, carbon atoms, for example methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl or amyl, and methoxy, ethoxy or isopropoxy. Halogen is e.g. fluorine, bromine or, preferably, chlorine.

The term "sulfo" denotes the sulfonic acid group. Aryl is preferably phenyl and aralkyl is preferably benzyl.

Alkyl groups within the definitions of X, R_1, R_2, R_3 and R_4 can be in straight chain or branched chain configuration. These alkyl groups may contain 1 to 12, preferably 1 to 5 and, most preferably, 1 to 3, carbon atoms. Examples of such alkyl groups are methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, n-hexyl, n-octyl or n-dodecyl.

Lower alkoxy-lower alkyl groups R_1, R_2, R_3 and R_4 are in particular alkoxyalkyl groups containing a total of 2 to 4 carbon atoms, e.g. β-methoxyethyl or β-ethoxyethyl.

X as cycloalkyl is e.g. cyclopentyl or, preferably, cyclohexyl. X as aralkyl is phenylethyl or, preferably, benzyl, whilst aryl will preferably be understood as denoting naphthyl, diphenyl and in particular, phenyl. The aralkyl and aryl radicals can be substituted by halogen, lower alkyl, lower alkoxy or sulfo.

Preferred substituents in the phenyl and benzyl nucleus of the radical X and of the radicals R are e.g. halogen, lower alkyl or lower alkoxy, for example chlorine, methyl or methoxy.

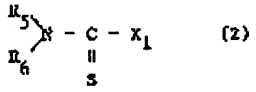
A heterocyclic radical represented by each pair of substituents (R_1 and R_2) and (R_3 and R_4), together with the nitrogen atom to which said pair is attached, is e.g. pyrrolidino, piperidino, pipecolino, morpholino or thiomorpholino.

Where R_1 and R_3 together are alkylene of 2 or 3 carbon atoms, they form together with the nitrogen atom to which they are attached a cyclic thiourea e.g. ethylene thiourea or propylene thiourea. Where R_1 and R_3 together are phenylene, they form, together with the thioureido grouping, phenylenethiourea which can be substituted by R_2 and R_4. Thiouracil-2 can also be used as cyclic thiocarbamide.

The substituent X is preferably a lower alkyl group or, preferably, a R_3R_4 N-group. R_1, R_2, R_3 and R_4 are preferably hydrogen or such is a lower alkyl group such as methyl or ethyl.

A cation M can be e.g. hydrogen, an alkali metal, preferably sodium or potassium, an alkaline earth metal, preferably magnesium or calcium, or an ammonium group. The term "ammonium group" as used here refers both to ammonium (NH_4^+) and to substituted ammonium groups. Those latter are derived e.g. from aliphatic amines such as di- or triethylamine or mono-, di- or triethanolamine, or from cycloaliphatic amines such as cyclohexylamine. The preferred meaning of M is hydrogen, an alkali metal or ammonium.

In the practice of this invention it is preferred to use compounds of the formula



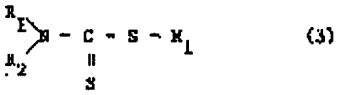
(2)

wherein X_1 is lower alkyl or  , and each of R_5, R_6, R_7 and

R_6 independently is hydrogen or lower alkyl. X_1 can preferably also be phenyl.

Especially preferred compounds of formula (2) are those in which X_1 is methyl, NH_2 or $-N(CH_3)_2$, and R_5 and R_6 are hydrogen or methyl. Typical examples of such compounds are thioacetamide, thiobenzamide, tetramethylthiourea and, in particular, thiourea.

Particularly suitable compounds are also dithiocarbamates of the formula



(3)

wherein R_1 and R_2 have the given meanings and X_1 is an alkali metal or ammonium.

In formula (3) above, R_1 and R_2 are preferably lower alkyl such as methyl or ethyl. The most important compound of this group is sodium diethyldithiocarbamate. Examples of further thiocarbamates are piperidine sodium dithiocarbamate or diethylammonium diethyldithiocarbamate.

In the process of this invention, the compounds of formulae (1) to (3) are employed primarily as additives for obtaining wood pulp from lignocellulose materials. Where these compounds have the indicated kappa-number (Tappy-System T-236 M-60), satisfactory yields of wood pulp are obtained therewith.

The amounts in which the compounds of formulae (1) to (3) are employed in the pulp liquors vary from 0.001 to 5 % by weight, preferably from 0.001 to 2.5 % by weight, based on the lignocellulose material.

The said thioamides, thiocarbamides, thiocarbamates and dithiocarbamates are employed by themselves or, preferably, in combination with an organic cyclic compound containing keto and/or hydroxyl groups.

Examples of suitable organic cyclic compounds containing keto and/or hydroxyl groups are monocyclic, dicyclic and/or polycyclic compounds, especially dicyclic, tricyclic and/or tetracyclic compounds, which contain two keto groups and/or two hydroxyl groups. Preferred compounds are 1,4-naphthoquinone, 9,10-anthraquinone, Diels-Alder adducts of 1,3-dienes, e.g. of unsubstituted or substituted butadiene with p-benzoquinone and/or 1,4-naphthaquinone, and/or the monoalkyl, dialkyl, hydroxy, amino, alkoxy, alkylamino, halogen and/or sulfo derivatives thereof.

It is possible to use e.g. the following compounds concurrently: 9,10-anthraquinone, 2-methylanthraquinone, 2-ethylanthraquinone, dichloroanthraquinone, 2,3-dimethylanthraquinone, 2,6-dimethylanthraquinone, 2,7-dimethylanthraquinone, 2-aminoanthraquinone, 1-methoxyanthraquinone, 2-methoxyanthraquinone, anthraquinone-2-sulfonic acid or anthraquinone-disulfonic acid (in the form of alkali metal salts), 1,2-benzanthraquinone, phenanthrenequinone, anthrone, 10-methylenanthrone, dihydroxyanthracene, dihydroxyanthracenesulfonate, tetrahydro-9,10-diketoanthracene or 1,3-dimethyl-tetrahydro-9,10-diketoanthracene. Two or more of these keto compounds can be used in the process of the invention. It is preferred to employ only one of these compounds and most preferred to employ 9,10-anthraquinone or 2-methyl-9,10-anthraquinone, together with the said thioamides, thiocarbamides or dithiocarbamates.

In the process of this invention there may be used e.g. 50 to 95% by weight of one or more organic cyclic compounds containing keto and /or hydroxyl groups, especially 9,10-anthraquinone, and

5 to 50 % by weight of one or more of the compounds of formulae (1) to (3). It is advantageous to use mixtures of 60 or, preferably, 70 to 90 % by weight of a cyclic compound containing keto and/or hydroxyl groups, preferably 9,10-anthraquinone or 2-methylanthraquinone, and 10 to 40 % by weight, preferably 10 to 30 % by weight, of a compound of formula (1) to (3), in particular thiourea, thioacetamide, tetramethylthiourea or sodium diethyldithiocarbamate.

Interesting mixtures are those of thiourea and anthraquinone, which are employed in the ratio of 1:3 or preferably, of 1:9 to 3:7.

The amounts in which the mixtures of compounds of formulae (1) to (3) and the cyclic compounds containing keto and/or hydroxyl groups are added to the pulp liquors, vary from 0.001 to 1 % by weight, preferably from 0.001 to 0.2 % by weight, based on the lignocellulose material.

The preferred lignocellulose material is wood. This is first usually converted into chips or shavings. The wood can be softwood, e.g. silver fir, spruce or pine, or hardwood, e.g. maple, birch, beech, oak, aspen or poplar. The lignocellulose material can, however, also be in fibrous form.

The chemical process for obtaining wood pulp is conveniently carried out in alkaline medium, e.g. by the sulfate or Kraft process, by the soda process, the sulfite cook under semialkaline conditions, or by the oxygen-alkali process. In this last mentioned process, the oxygen can be introduced before or after the treatment with alkali. Another possible method of obtaining chemical pulp which can be employed in this invention is the polysulfide process. This process can be carried out both in alkaline and in neutral medium. The sulfite pulping process in neutral medium can be carried out in particular using the said mixtures of the thio compounds and the

cyclic keto compounds. Further, the lignocellulose material can be cooked in a first step in the presence of sodium hydroxide, the treated material beaten, and the beaten material subjected to a second cooking step which is carried out in the presence of an alkaline solution of a peroxide, e.g. hydrogen peroxide, or of an alkali peroxide.

The pulping process of this invention can be carried out at a temperature of 50° to 250°C, preferably from 120° to 200°C. The pulping process is carried out at a ratio of lignocellulose material to cooking liquor of 1:3 to 1:50, preferably from 1:3 to 1:10.

It is preferred to treat lignocellulose material in a closed vessel at a liquor ratio of 1:3 to 1:10 with an alkali preparation which contains 0.001 to 0.2 % by weight of a mixture of a compound of formulae (1) to (3) and an anthraquinone compound, based on the lignocellulose material. The preferred alkali is sodium hydroxide and/or magnesium hydroxide, which is normally employed in the form of a 2 to 15 % aqueous solution. Very good results are also obtained with a combination of the said sodium hydroxide solution with sodium sulfide by the Kraft process. Sodium sulfide is advantageously employed in an amount of 0.01 to 40 g/l, preferably from 0.1 to 25 g/l.

Compared with the processes using anthraquinone alone as known delignifying agent, the process of this invention, especially when using the said mixture, produces pulps which give paper having better strength properties. Owing to the synergistic action of the mixture employed, it is possible in particular to reduce the amount of expensive anthraquinone derivative, while the yield and rate of delignification remain virtually unchanged.

In the following Examples the chlorine number is determined as

references value for the residual content of lignin and the yields are calculated. Parts and percentages are by weight.

Examples 1 to 3: Three samples of mill chips (Picea abies, maximum thickness = 3 mm), each having a weight of 25 g, are treated in an autoclave at 80°C with 100 ml of aqueous 1.18 N sodium hydroxide solution and then scavenged with nitrogen. Each alkaline mixture is then treated with one of the mixtures listed in column 2 of Table 1 and consisting of thiourea and 9,10-anthraquinone in the indicated percentage amount (column 3) and ratio (column 4), whereupon the temperature is raised to 173°C and the mixture is kept for two hours at this temperature. After cooling, the crude pulp is filtered off, washed with hot water and rinsed with deionised water. The pulp is then beaten and pressed to a sheet. The average chlorine number and the average yields of the three experiments of the individual Examples are determined. The data are reported in Table 1. The percentage yield of pulp, based on the wood employed, is indicated in the second last column of the table. The lignin content of the pulps is calculated by multiplying the chlorine consumption by the factor 0.90 in accordance with the Scandinavian Pulp, Paper and Board Testing Committee (Scan-C 29:72). The chlorine number is given in column 5 of the table. The hydrocarbon content of the pulps is determined from the difference of the pulp yield and the lignin content. Accordingly, the lignin-free yield is given in the last column of the table.

Table 1

1	2	3	4	5	6	7
Example	Additive	Amount in %	Ratio	Chlorine number	Pulp yield in %	Lignin-free pulp yield in %
1	thiourea / anthraquinone	0.03	1 : 9	9.5	49	44.8
2	thiourea / anthraquinone	0.05	2 : 8	9.5	49.1	44.9
3	thiourea / anthraquinone	0.05	3 : 7	9.8	49.2	44.8
	anthraquinone	0.05	—	9.1	48.7	44.7

Examples 4 to 6: Three samples of mill chips, each weighing 25 g, are treated in an autoclave at 80°C with 100 ml of an aqueous 1.1N sodium hydroxide solution and 1.13 g of sodium sulfide and scavenged with nitrogen. To each alkaline mixture is then added one of the mixtures listed in column 2 of Table 2 and consisting of thiourea and 9,10-anthraquinone in the percentage amount indicated in column 3 and in the ratio indicated in column 4, whereupon the temperature is raised to 166°C and the cooking mixture is then kept for 2 hours at this temperature. After cooling, the crude pulp is filtered off, washed with hot water, and rinsed with deionised water. The pulp is then beaten and pressed to a sheet. The chlorine number and the yields of the individual experiments and the average of the three experiments are then determined. The results are reported in Table 2. The chlorine number is indicated in column 5, and the pulp yield and lignin-free yield are stated in columns 6 and 7 respectively (in %, based on the wood employed).

Table 2

1	2	3	4	5	6	7
Example	Additive	Amount in %	Ratio	Chlorine number	Pulp yield in %	Lignin-free pulp yield in %
4	thiourea / anthraquinone	0.05	1 : 9	8.0	48.5	45.0
5	thiourea / anthraquinone	0.05	2 : 8	8.0	48.7	45.2
6	thiourea / anthraquinone	0.05	3 : 7	8.1	48.6	45.1
	anthraquinone	0.05	---	8.8	48.9	45.2

Examples 7 to 9: Three samples of mill chips, each weighing 25 g, are treated in an autoclave at 80°C with 100 ml of an aqueous 1N sodium hydroxide solution and 2 g of sodium sulfide and scavenged with nitrogen. To each alkaline mixture is then added one of the mixtures listed in column 2 of Table 3 and consisting of thiourea and 9,10-anthraquinone in the percentage amount indicated in column 3 and in the ratio indicated in column 4, whereupon the temperature is raised to 168°C and the cooking mixture is then kept for 2 hours at this temperature. After cooling, the crude pulp is filtered off, washed with hot water, and rinsed with deionised water. The pulp is then beaten and pressed to a sheet. The chlorine number and the yields of the individual experiments and the average of the three experiments are then determined. The results are reported in Table 3. The chlorine number is indicated in column 5, and the pulp yield and lignin-free yield are stated in columns 6 and 7 respectively (in %, based on the wood employed).

Table 3

1	2	3	4	5	6	7
Example	Additive	Amount in %	Ratio	Chlorine number	Pulp yield in %	Lignin-free pulp yield in %
7	thiourea / anthraquinone	0.05	1 : 9	6.4	46.0	45.2
8	thiourea / anthraquinone	0.05	2 : 8	6.4	48.1	46.3
9	thiourea / anthraquinone	0.05	3 : 7	6.6	47.9	45.0
	anthraquinone	0.05	---	6.5	47.7	44.9

Example 10: Three samples of mill chips, each weighing 25 g, are treated in an autoclave at 80°C with 100 ml of an aqueous 1.18N sodium hydroxide solution and scavenged with nitrogen. On the one hand, no additive is added to the alkaline mixtures and, on the other, thiourea and 9,10-anthraquinone are added in the percentage amounts indicated in column 2 of Table 4. The temperature is then raised to 173°C and the cooking mixtures are then kept for 2 hours at this temperature. After cooling, the crude pulp is filtered off, washed with hot water, and rinsed with deionised water. The pulp is then beaten and pressed to a sheet. The chlorine number and the yields of the individual experiments and the average of the three experiments are then determined. The results are reported in Table 4. The chlorine number is indicated in column 3, and the pulp yield and lignin-free yield are stated in columns 4 and 5 respectively (in %, based on the wood employed). It is evident from this Example that thiourea can also be used alone to increase the selectivity of the process. However, it requires about 40 times more

thiourea than anthraquinone to achieve this ammo effect. The fact that the same effect is achieved with a mixture of up to 30 % of thiourea and 70 % of anthraquinone as with pure anthraquinone (see Examples 1 to 9) shows therefore that the combination of these additives produces a synergistic effect.

Table 4

1	2	3	4	5
Additive	Amount in %	Chlorine number	Pulp yield in %	Lignin-free pulp yield in %
without additive		17.5	50.5	42.4
thiourea	1	11.9	48.6	43.4
thiourea	2	10.2	48.0	46.3
anthraquinone	0.04	10.1	47.9	43.5

Examples 11 to 20: Two samples of mill chips, each weighing 25 g are treated in an autoclave at 80°C with 100 ml of an aqueous 1.11BN or 1.123N sodium hydroxide solution and scavenged with nitrogen. Then, on the one hand, no addition of additive or the addition of anthraquinone is made to each alkaline mixture, and on the other hand, tetramethylthiourea, ethylene thiourea, benzothionmide or sodium diethyldithiocarbamate is added in the respective amount indicated in column 3 of Table 5, whereupon the temperature is raised to 175°C and the cooking mixture is then kept for 2 hours at this temperature. After cooling, the crude pulp is filtered off, washed with hot water, and rinsed with deionised water. The pulp is then beaten and pressed to a sheet. The chlorine number and the yields of

the individual experiments and the average of the two experiments are then determined. The results are reported in Table 5. The chlorine number is indicated in column 5, and the pulp yield and lignin-free yield are stated in columns 6 and 7 respectively (in %, based on the wood employed).

Table 5

1	2	3	4	5	6	7
Ex.	Additive	Amount in %	NaOH concentration	Chloride number	Pulp yield in %	Lignin-free pulp yield in %
11	tetramethyl thiourea	0.36	1.123-N	17.7	53.2	46.7
12	tetramethyl thiourea	0.64	1.123-N	15.6	51.7	44.5
13	tetramethyl thiourea	1.00	1.123-N	16.1	51.6	45.1
14	tetramethyl thiourea	1.44	1.123-N	12.9	50.7	44.8
15	ethylene thiourea	1.0	1.123-N	16.4	52.9	45.1
16	benzothioamide	1.0	1.123-N	16.2	52.5	44.9
	without additive	-	1.123-N	21.6	55.6	46.8
	anthraquinone	0.04	1.123-N	18.2	49.9	44.8
17	Na-diethyldithiocarbamate	0.36	1.118-N	15.8	51.3	44.0
18	Na-diethyldithiocarbamate	0.64	1.118-N	14.3	50.6	44.2
19	Na-diethyldithiocarbamate	1.00	1.118-N	12.1	49.5	44.1
20	Na-diethyldithiocarbamate	1.44	1.118-N	11.3	49.2	44.2
	anthraquinone	0.04	1.118-N	11.0	49.0	44.2

Examples 21 to 35: Two samples of mill chips, each weighing 25 g, are treated in an autoclave at 80°C with 100 ml of an aqueous 1.116N or 1.126N sodium hydroxide solution and scavenged with nitrogen. Then, on the one hand, anthraquinone is added to each alkaline mixture, and on the other hand, ethylene thiourea, thioacetamide, thiobenzamide or thiouracil-2 is added in the respective amount indicated in column 3 of Table 6, whereupon the temperature is raised to 173°C and the cooking mixture is then kept for 2 hours at this temperature. After cooling, the crude pulp is filtered off, washed with hot water, and rinsed with deionised water. The pulp is then beaten and pressed to a sheet. The chlorine number and the yields of the individual experiments and the average of the two experiments are then determined. The results are reported in Table 6. The chlorine number is indicated in column 5, and the pulp yield and lignin-free yield are stated in columns 6 and 7 respectively (in %, based on the wood employed).

Table 6

1 Ex.	2 Additive	3 Amount in %	4 NaOH concentration	5 Chlorine number	6 Pulp yield in %	7 Lignin-free yield in %
21	ethylenethiourea	0.16	1.122 N	16.81	52.38	44.45
22	ethylenethiourea	0.64	1.122 N	13.58	50.82	44.61
23	ethylenethiourea	1.44	1.122 N	11.35	49.62	44.53
24	ethylenethiourea	2.56	1.122 N	10.85	49.75	44.89
25	thioacetamide	0.16	1.126 N	16.52	54.47	46.37
26	thioacetamide	0.64	1.126 N	12.71	52.49	46.49
27	thioacetamide	1.44	1.126 N	9.78	51.06	46.93
28	thioacetamide	2.56	1.126 N	9.22	51.46	47.19
29	thiobenzamide	0.16	1.126 N	18.02	56.14	47.04
30	thiobenzamide	0.64	1.126 N	15.08	54.24	46.88
31	thiobenzamide	1.44	1.126 N	12.29	52.81	46.97
32	thiobenzamide	2.56	1.126 N	10.18	51.82	47.05
33	thiouracil-2	0.16	1.116 N	18.32	55.47	46.32
34	thiouracil-2	0.64	1.116 N	16.13	54.75	45.80
35	thiouracil-2	1.44	1.116 N	15.45	54.75	47.14
	anthraquinone	0.04	1.122 N	16.13	49.42	44.32

Examples 36 to 41: Three samples of mill chips, each weighing 25 g, are treated in an autoclave at 80°C with 100 ml of an aqueous 1.1ON sodium hydroxide solution (additionally with 11 g/l of Na_2S in Examples 39 - 41) and scavenged with nitrogen. To each alkaline mixture is then added, on the one hand, anthraquinone or 2-methyl-anthraquinone, and on the other, thiourea, thiourea/2-methyl-anthraquinone (1:4), thiourea/anthraquinone (1:3), thioacetamide/anthraquinone (1:3), in the respective percentage amounts indicated in column 2 of Table 7, whereupon the temperature is raised to 175°C (166°C in Examples 39-41) and the cooking mixture is kept for 2 hours at this temperature (53 minutes in Examples 39-41). After cooling, the crude pulp is filtered off, washed with hot water, and rinsed with deionised water. The pulp is then beaten and pressed to a sheet. The chlorine number and the yields of the individual experiments and the average of the three experiments are then determined. The results are reported in Table 7. The chlorine number is indicated in column 5, and the pulp yield and lignin-free yield are stated in columns 6 and 7 respectively (in %, based on the wood employed).

Table 2

1	2	3	4	5	6	7
Ex.	Additive	Amount in %	NaOH concentration	Chlorine number	Pulp yield in %	Lignin-free yield in %
36	anthraquinone	0.05	1.10 N	10.28	49.37	44.89
37	thioacetamide/ anthraquinone(1:3)	0.05	1.10 N	10.38	49.39	44.69
38	thiourea/ anthraquinone(1:3)	0.05	1.10 N	10.81	49.53	44.80
39	2-methylanthraquinone	0.01	1.10 N	6.06	51.10	48.31
40	thiourea/2-methyl-anthraquinone(1:4)	0.01	1.10 N	6.24	50.99	48.13
41	-	-	1.10 N	8.82	51.87	47.75

Examples 36 - 38 : soda process

Examples 39 - 41: Kraft process with 20 % sulfide content

Examples 42 to 53: Three samples of wood chips, each weighing 25 g, are treated in an autoclave at 80°C with 100 ml of an aqueous 1.10N sodium hydroxide solution (additionally with 11 g/l of Na_2S in Examples 46 - 49 and with 40.6 g/l of Na_2S in Examples 50 - 53) and scavenged with nitrogen. To each alkaline mixture is then added, on the one hand, anthraquinone and on the other, thiourea or thiourea/anthraquinone (1:3) in the respective percentage amounts indicated in column 3 of Table 8, whereupon the temperature is raised to 160°C (150°C in Examples 46 - 53) and the cooking mixture is kept for 90 minutes at this temperature (45 minutes in Examples 46 to 53). After cooling, the crude pulp is filtered off, washed with hot water, and rinsed with deionized water. The pulp is then beaten and pressed to a sheet. The chlorine number and the yields of the individual experiments and the average of the three experiments are then determined. The results are reported in Table 8. The chlorine number is indicated in column 5, and the pulp yield and lignin-free yield are stated in columns 6 and 7 respectively (in %, based on the wood employed). In addition, a part of the pulp is bleached and the viscosity of the pulp is determined. The values are reported in column 8 of the table.

Table 8:

1	2	3	4	5	6	7	8
Ex.	Additive	Amount in %	NaOH concentration	Chlorine number	Pulp yield in %	Lignin-free yield in %	Intrinsic viscosity *)
42	-	-	1.10 N	14.21	57.65	50.45	1231
43	anthraquinone	0.10	1.10 N	4.32	53.83	51.74	1167
44	thiourea	0.10	1.10 N	13.36	57.52	50.60	1251
45	thiourea/anthraquinone (1:3)	0.10	1.10 N	4.15	53.81	51.80	1209
46	-	-	1.10 N	14.17	57.18	48.89	1311
47	anthraquinone	0.10	1.10 N	8.13	54.27	50.30	1353
48	thiourea	0.10	1.10 N	13.78	57.23	50.13	1424
49	thiourea/anthraquinone (1:3)	0.10	1.10 N	7.83	55.75	50.06	1352
50	-	-	0.995 N	9.06	54.33	49.72	1503
51	anthraquinone	0.10	0.995 N	5.57	52.73	50.09	1486
52	thiourea	0.10	0.995 N	8.75	53.81	49.57	1527
53	thiourea/anthraquinone (1:3)	0.10	0.995 N	5.53	52.73	50.11	1406

Examples 42 - 45 : soda process

Examples 46 - 49 : Kraft process with 20 % sulfide content

Examples 50 - 53 : Kraft process with 34 % sulfide content

*) determined in accordance with the Scandinavian Pulp, Paper and Board Testing Committee, SCAN-C 25:62

Examples 54 to 57: 700 g of mill chips (absolute dry) obtained from spruce (picea excelsa) are put into an autoclave at 80°C with 2.8 litres of cooking liquor. The cooking liquor is specified in Table 9. The temperature is raised 1°C per minute to 173°C (Examples 54 - 56) or 168°C (Example 57) and the cooking mixture is kept at this temperature for 2 hours (Examples 54 - 56) or 1 hour (Example 57). The cooking mixture is then cooled and each pulp is worked up in the conventional manner and analysed. The data are reported in Table 9. In addition, the pulp is beaten (each pulp at 6 different degrees of beating) and the corresponding physical properties are determined. The results are summarised in Tables 10 to 13, in which for comparison purposes the values for tear strength are set against those for the corresponding breaking length. From the relation of tear strength to breaking length it is seen that the pulps of Examples 54 and 55 have about the same strength properties, although the kappa-number of Example 55 is somewhat higher. In addition, it is to be noted that the graded yield of Example 55 is about 3.7 % higher. It is evident from the difference in the lignin-free yields (2.6 %) that this increase in yield is attributable to a higher carbohydrate yield. The proportion of rejects of Example 55 is somewhat better than that of Example 54. The viscosity is also improved.

If the tear strength values are compared with the corresponding breaking length values of the pulps obtained in Examples 54 and 57 (Kraft process: .20 % sulfide content), the following conclusion may be drawn: the pulp cooked with thiourea has better strength properties than that cooked with anthraquinone, although the lignin content is higher. This is also in accord with the higher viscosity; the yield is improved. Strength properties, viscosity and lignin-free yield of the pulp obtained in Example 56 are comparable with the corresponding properties of a pulp obtained by a Kraft process as described in Example 57 (sulfide content c. 2 %), although the sulfide content, which at best is afforded by the thioureas, is only half as high (c. 10 %).

Table 9

Example	Additive	Amount in %	Cooking NaOH m/l	liquor Na_2S m/l	Temperature °C	Kappa	Chlorine number	Rejects in %	Total yield in %	Graded yield in %	Lignin free yield	Viscosity m Pas
54	anthraquinone	0.05	1.12	—	173	64.7	10.0	2.9	50.6	47.7	43.4	24.5
55	thiourea/anthra-quinone (1:1)	0.05	1.12	—	173	76.3	11.7	2.6	54.0	51.4	46.0	26.5
56	thiourea	2.0	1.12	—	173	82.2	12.7	2.8	53.6	50.8	45.0	36.7
57	---	—	1.00	0.142	168	70.2	10.9	2.9	52.6	49.7	44.8	41.1

Table 30: Strength properties of Example 54

PHYSICAL ANALYSIS							
Based on 40°C SR	Beating in a Jokro mill: per 16 g abs. dry, pulp, 150 rpm (tested at 50 % rel. humidity and 23°C) sheet formation: Rapid-Köthen						
48.5	beating time in minutes	0	15	25	40	60	
40	freeness, °SR	16	16	20	28	55	
8450	breaking length, m	6600	7000	7300	8150	9150	
5.43	bursting pressure $\frac{kPa\ m^2}{g}$ (SCAN)	4.65	4.30	5.25	5.00	5.90	
1320	tear, cN (Elmendorf)	2640	1720	1640	1440	1180	

Table II: Strength properties of Example 55

PHYSICAL ANALYSIS							
Based on 40° SR	Beating in a Jokro mill: per 16 g abs. dry, pulp, 150 rpm (tested at 50 % rel. sheet formation: Rapid-Köthen humidity and 23°C)						
50	beating time in minutes	0	15	25	40	60	
40	freeness, ° SR	15	26	17	27	54	
8400	breaking length, m	5430	6850	7750	7700	8750	
5.10	bursting pressure $\frac{kPa\ m^2}{g}$ (SCAN)	3.20	3.95	4.65	4.50	5.40	
	tear, mN (Elmendorf)	2500	1625	1960	1560	1130	

Table 12: Strength properties of Example 56

PHYSICAL ANALYSIS								
based on 40° SR	Beating in a Jokro mill: per 16 g abs. dry, pulp. 350 rpm (tested at 50 2 rel. sheet formation: Rapid-Köthen humidity and 23°C)							
47	Beating time in minutes	0	15	25	40	60		
40	freeness, ° SR	16	17	19	29	60		
9200	breaking length, m	7050	8650	9000	9750	10150		
6.45	bursting pressure $\frac{kPa\ m^2}{g}$ (SCAN)	4.60	5.60	6.30	6.10	6.50		
1100	tear, mN (Elmendorf)	2100	1470	1250	1220	990		

Table 13: Strength properties of Example 57

PHYSICAL ANALYSIS								
Based on 40° SR	Beating in a Jokro mill: per 15 g abs. dry, pulp, 150 rpm (tested at 50 % rel. humidity and 23°C) sheet formation: Rapid-Köthen							
50	beating time in minutes	0	15	25	40	60		
60	freeness, ° SR	16	17	20	25	54		
9900	breaking length, m	7000	8000	9450	9600	10200		
6.55	bursting pressure $\frac{kPa\ m^2}{g}$ (Mullen)	5.30	5.50	5.85	6.30	6.70		
Load	tear, mN (Elmendorf)	1770	1620	1400	1280	1170		

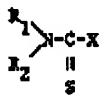
The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for delignifying lignocellulose material by chemical pulping, which process comprises carrying out the pulping operation at a temperature up to 250°C in the presence of an effective amount of a thioamide, thiocarbamide, thiocarbamate or dithiocarbamate, wherein the ratio of the lignocellulose material to the pulping liquor is in the range of 1:3 to 1:50.

2. A process according to claim 1 which comprises the use of a cyclic or acyclic thiocarbamide or dithiocarbamate.

3. A process according to claim 2 which comprises the use of an acyclic thiourea.

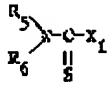
4. A process according to claim 1 which comprises the use of a compound of the formula



(1)

wherein X is alkyl of 1 to 12 carbon atoms, cycloalkyl, aryl, aralkyl,  , -OM or -SM, each of R_1, R_2, R_3 and R_4 independently is hydrogen, alkyl of 1 to 12 carbon atoms, lower alkoxy-lower alkyl, phenyl, benzyl, or phenyl or benzyl substituted by halogen, lower alkyl, lower alkoxy, lower alkoxy-lower alkyl or sulfo, or each pair of substituents (R_1 and R_2) and (R_3 and R_4) independently, together with the nitrogen atom to which said pair is attached, is a 5- or 6-membered heterocyclic radical, or R_1 and R_3 together are alkylene of 2 or 3 carbon atoms or phenylene, and M is a cation.

5. A process according to claim 4 which comprises the use of a compound of the formula

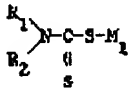


(2)

wherein X_1 is lower alkyl, phenyl or  and each of R_5, R_6, R_7 and R_8 independently is hydrogen or lower alkyl.

6. A process according to claim 5 which comprises the use of a compound of formula (2), wherein X_1 is methyl, $-NH_2$ or $-N(CH_3)_2$ and R_5 and R_6 are hydrogen or methyl.

7. A process according to claim 4 which comprises the use of a compound of the formula



(3)

wherein each of R_1 and R_2 independently is hydrogen, alkyl of 1 to 12 carbon atoms, lower alkoxy-lower alkyl, phenyl, benzyl, or phenyl or benzyl substituted by halogen, lower alkyl, lower alkoxy, lower alkoxy-lower alkyl or sulfo, or R_1 and R_2, together with the nitrogen atom to which they are attached, are a 5- or 6-membered heterocyclic radical and M_1 is an alkali metal or ammonium.

8. A process according to claim 7 which comprises the use of a compound of the formula (3), wherein R_1 and R_2 are lower alkyl.

9. A process according to claim 1 which comprises the use of an organic cyclic compound containing keto or hydroxyl groups or a mixture of these groups in addition to the thioamide, thiocarbamide, thiocarbazate or dithiocarbamate.

10. A process according to claim 9, wherein the additional compound is a dicyclic, tricyclic or tetracyclic compound or a mixture thereof containing two keto groups or two hydroxyl groups or a mixture of these groups.

11. A process according to claim 10, wherein the additional compound is anthraquinone or 2-methylanthraquinone.

12. A process according to claim 9, wherein the cooking liquor contains a mixture of 50 to 95 % by weight of one or more of said organic cyclic compounds, and 5 to 50 % by weight of one or more compounds of the formula (1) as defined in claim 4.

13. A process according to claim 9, wherein the cooking liquor contains 70 to 90 % by weight of said organic cyclic compound and 10 to 30 % by weight of a compound of the formula (1) as defined in claim 4.

14. A process according to claim 9, wherein the cooking liquor contains a mixture of thiourea and anthraquinone or a mixture of thiourea and 2-methyl-anthraquinone, each mixture being in the ratio of 1:3 or 1:4.

15. A process according to claim 9, wherein the cooking liquor contains a mixture of thiourea and anthraquinone in the ratio of 1:9 to 3:7.

16. A process according to claim 1, wherein pulping is carried out in the temperature range from 50° to 250°C.

17. A process according to claim 16, wherein pulping is carried out in the temperature range from 120° to 200°C.

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EINSCHLÄGIGE DOKUMENTE

Kategorie	Kennzeichnung des Dokuments mit Angabe, soweit erforderlich, der maßgeblichen Teile	betrifft Anspruch
X	ABSTRACT BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY, Band 48, Nr.11, Mai 1978, Seite 1187, Zusammenfassung 11073 Appleton, Wisc. US B.I. FLEMING et al. "Reducing agents as additives for soda pulping" & SVENSK PAPPERSTID. 81, no. 1, 13-18 (Jan. 25, 1978) * Im Ganzen *	1-5, 15
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KLASSIFIKATION DER ANMELDUNG (Int. Cl.³)

D 21 C 3/00

RECHERCHIERTE SACHGEBIETE (Int. Cl.³)

D 21 C 3/00

KATEGORIE DER GENANNTEN DOKUMENTE

- X: von besonderer Bedeutung
- A: technologischer Hintergrund
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- &: Mitglied der gleichen Patentfamilie, übereinstimmendes Dokument

X Der vorliegende Recherchenbericht wurde für alle Patentansprüche erstellt.

Recherchenort	Abschlußdatum der Recherche	Prüfer
Den Haag	24-12-1981	NESTBY

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Kategorie	Kennzeichnung des Dokuments mit Angabe, soweit erforderlich, der Maßgeblichen Teile	betrifft Anspruch
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A	TAPPI, JOURNAL OF THE TECHNICAL ASSOCIATION OF THE PULP AND PAPER INDUSTRY, Band 51, Nr. 2, Februar 1978 Atlanta, Ga, US L. LOWENDAHL et al."Carbohydrate stabilization during soda pulping with addition of anthraquinone" Seiten 19-21. ----	1,10, 15

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